IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

Appln. No:	10/017,367
Applicant:	Kevin K. Lehmann et al.
Filed:	December 12, 2001
Title:	FIBER OPTIC BASED CAVITY RING-DOWN SPECTROSCOPY APPARATUS
TC/A.U.:	2877
Examiner:	Pham, Hoa Q.
Docket No.:	PRU-101US

DECLARATION UNDER 37 C.F.R. §1.131

Commissioner for Patents
P.O. Box 1450
Alexandria, VA 22313-1450

Sir:

We, Kevin K. Lehmann, Peter B. Tarsa, and Paul Rabinowitz, hereby declare that:

1. We are the co-inventors of the subject matter of the patent application identified above and are familiar with the contents of that patent application.

2. The purpose of this declaration, which is submitted before final rejection of the subject patent application, is to establish completion of the invention of the subject matter disclosed in the application in the United States at a date before the effective date of U.S. Patent Publication US 2003/007715 (the '715 publication).

3. All of the acts described in this declaration took place within the United States.

4. At the time of our contribution to the conception and reduction to practice of the invention, each of us inventors was an employee of or a student enrolled at Princeton University, the assignee of the present invention.

5. We conceived of the invention disclosed and claimed in the subject application before the effective date of the '715 publication.

6. The invention was submitted as part of a draft proposal to the General Exams Committee of the University before the effective date of the '715 publication.

7. Still before the effective date of the '715 publication, an oral defense of the proposal was heard by the General Exams Committee.

8. Yet, still before the filing date of the '715 publication, the University approved the proposal.

9. We next submitted an Invention Disclosure form disclosing our invention to the Legal Department of Princeton University, still before the filing date of the '715 publication.

10. Still before the filing date of the '715 publication, the Princeton Legal Department received our Invention Disclosure form and began evaluation of the merits of our invention to determine whether to file a patent application.

11. The Princeton Legal Department subsequently completed its evaluation and requested that the law firm of RatnerPrestia prepare a patent application covering our invention of a fiber optic based cavity ring-down spectroscopy apparatus.

12. A draft application was completed by RatnerPrestia, reviewed and revised by us as the inventors. The final draft application was submitted to us for final review and approval. RatnerPrestia then proceeded to file the subject patent application in the United States Patent and Trademark Office.

13. From the time of conception and reduction to practice, we diligently worked with our patent attorneys to prepare and file the subject patent application. At no time was the invention abandoned, suppressed, or concealed.

14. The invention covered in the subject patent application was neither disclosed to anyone outside of Princeton University without a confidentiality agreement nor on sale or in public use more than one year before the filing of the application.

15. That Exhibits 1 and 2 represent documents internal to Princeton University and were created and distributed in a confidential manner.

16. That from the above statements and the documents contained in Exhibits 1 and 2, it can be seen that the invention in this application was made before the earliest effective date of the '715 publication.

17. That the following exhibits are attached to this Declaration:

EXHIBIT	DESCRIPTION
1	Proposal
2	General Examination Report

18. By each of our signatures below, we hereby declare that all statements made in this document of our own knowledge are true, and that all statements made on information and belief are believed to be true. Further, we hereby declare that these statements are made with the knowledge that willful false statements, and the like so made, are punishable by fine or imprisonment, or both, under Section 1001, Title 18 of the United States Code and that such willful false statements may jeopardize the validity of the application or any patent issuing on the application

Respectfully submitted,

Dated: 12/4/03

Kevin K. Lehmann

Dated: 12/4/2003

Peter B. Tarsa

Dated: 12/4/03

Paul Rabinowitz

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An Optical Fiber Resonator for the Trace Detection of Ammonia

A proposal submitted in partial fulfillment
of the requirements for a Ph.D. degree.
Chemistry Department, Princeton University

Peter Tarsa
May 2001

Background

Cavity ring-down spectroscopy (CRDS) is an established method for detection of trace quantities of gaseous species.[1] CRDS traditionally uses a near confocal resonator formed by two highly reflective mirrors. The rate of bulk molecular absorption is measured from the small fraction of light transmitted by the resonator, which decays exponentially in time. This rate is designated by $1/\tau$, defined as the inverse of the time to reach 1/e of the peak intensity, and it is directly proportional to the concentration of absorbing species.[1] The decay time is generally in the range of microseconds, allowing CRDS to also facilitate real time analysis.

Such long cavity decay times are due to the use of highly reflective mirrors to achieve high cavity finesse. These resonators achieve effective path lengths on the order of kilometers and enable the observation of weak absorption lines.[2] High signal-to-noise ratios complement this increase in sensitivity. Laser intensity fluctuations do not affect ring-down times, and under ideal conditions the shot noise generated by the signal in the detector is the only limit to the signal-to-noise ratio.[3] This enables quantitative detection in the range of parts per trillion of a range of gaseous molecules. Such sensitive detection has been demonstrated with ammonia.[4,5]

A need for trace detection of ammonia exists due to its importance in industrial production and atmospheric processes. Ammonia plays a substantial role in chemical production, such as in the manufacture of nitric acid, but it is nocuous to workers in concentrations above 25 ppm.[6] Chemical plant emissions also account for significant point source contributions of ammonia in the atmosphere.[7] Excess concentrations in the atmosphere disrupt the environmental nitrogen cycle and are especially toxic for plant life, as most plants have no excretion mechanism for ammonia.

The importance of ammonia regulation motivated the development of several fast detection methods for trace concentrations. Peeters *et al.* demonstrated the feasibility of Cavity-enhanced Absorption Spectroscopy (CAS) detection of 100 ppb of ammonia in one second in the 1.5μm region.[5] CAS uses a high finesse resonator composed of highly reflective mirrors similar to a ring-down cavity, but it compares the change in signal amplitude to a reference cell instead of measuring decay time. Recent work in the

Lehmann research group showed that ammonia detection by CRDS provides improved sensitivity compared to CAS. Using a continuous wave CRDS device, detection of 1.51 ppb was accomplished.[4] This is the lowest detection limit currently obtained for real time analysis of ammonia.

CRDS is the fastest, most sensitive technique, but it has several limitations. The dielectric mirrors used in the cavity have reflective coatings that span only narrow wavelength regions, making broadband scanning and detection impossible. CRDS suffers from excessive loss and decreased sensitivity in a scattering medium such as smoke or condensed vapor. In addition, mirror performance in corrosive environments has not been thoroughly tested and may further limit CRDS applicability. Despite the many applications of CRDS, little has been done to overcome these constraints.

Evanescent wave spectroscopy (EWS) does not suffer from the same obstacles as CRDS because it does not rely on the direct interaction of the propagating electromagnetic field with the analyte. EWS instead exploits the phenomenon of total internal reflection (TIR) and the resulting evanescent wave. When light impinges on a surface of lower index of refraction than the propagation medium at greater than a critical angle, it reflects completely.[8] A field exists, however, beyond the point of reflection that is non-propagating and decays exponentially with distance from the interface. This evanescent field carries no power in a pure dielectric medium, but attenuation of the reflected wave allows observation of the presence of an absorbing species in the region of the evanescent field.[9] EWS traditionally uses a waveguide as the propagation medium and either gaseous or thin film analytes for both qualitative and quantitative detection. EWS instruments are more flexible than ring-down cavities because of the durability of most waveguide materials and their broadband transmitting properties.

Pipino, *et al.* combined CRDS and EWS to create a sensitive detector for coatings on a prism based cavity.[10] A hexagonal prism facilitates detection of absorbers at four of the surfaces through attenuation of the evanescent field. Small prisms, in place of highly reflective mirrors, are used to couple light in and out of the resonator by photon tunneling and introduce broadband capabilities. A monolithic resonator effectively combines the versatility of an EWS instrument with the high sensitivity of CRDS.

There are several limitations of the monolithic resonator based on requirements of the prism materials. The prism surfaces need expensive superpolishing to minimize scattering losses. The prism material also exhibits high bulk scattering attenuation, which is the primary source of optical loss and cause of reduced sensitivity. Implementation of lower loss materials and improved interaction of the evanescent field with the absorber through an increased number of reflections counters these sources of diminished sensitivity. This enhancement could be accomplished through the use of an optical fiber as a propagation medium.

Blair and Chen demonstrated sensitivity enhancement in a waveguide-based cavity, similar to the monolithic prism resonator, for evanescent excitation of fluorescent molecules.[11] In their device, a cylindrical waveguide excites the so called "whispering gallery" modes in the resonator, which are essentially trapped waves in an axially symmetric waveguide.[12] These modes in turn excite fluorophores in the analyte. This technique shows output enhancement, with an increase in the signal-to-noise ratio by an order of magnitude, enabling the use of significantly smaller analyte volumes. Blair and Chen hypothesize that such a waveguide resonator could similarly be used for absorption spectroscopy.[11]

The waveguide resonator could further be improved with the implementation of optical fibers to create an efficient combination of EWS and CRDS. Commercially available telecommunications grade fiber optics enable adaptable design and increased durability in such an instrument. The increased number of reflections in an optical fiber compensates for the lack of a large surface area that is characteristic of a monolithic cavity. A mode-preserving fiber ensures that only the lowest order optical mode is present, enabling maximum interaction in the resonator of the evanescent field with the absorber.[13] This is not possible in an "overmoded" waveguide cavity, such as that used by Blair and Chen, because of the complex mode structure of the resonating whispering gallery modes. The utilization of optical fibers would create an absorption-detecting resonator with signal-to-noise ratios and limits of detection comparable to CRDS instruments.

Optical fibers have the lowest attenuation where telecommunications lasers operate, around 1550 nm. Ammonia has several strong overtone transitions in this

region,[15] which are suitable for detection by CRDS because of their strength and relatively narrow linewidth. Recent innovations in telecommunications technology lend themselves to such sensitive spectroscopic application, as optical fibers are designed to transmit signals over many kilometers with little attenuation. In addition, removal of the cladding that surrounds the fiber core permits the direct exposure of an optical fiber to a gaseous analyte.[14] Currently fiber splices are the main limitation on such a device, but present methods enable the generation of relatively low loss joints.

This proposal aims to build a fiber optic based resonator for quantitative measurement of ammonia at limits approaching that of traditional CRDS. Current research in trace detection spectroscopy suggests the practicality of such a detector both in terms of production and utilization. The low cost of telecommunications grade fiber optics would make such an instrument inexpensive to build and maintain. This device would also have a wide variety of applications due to the adaptable nature of optical fibers. A fiber based resonator could be miniaturized to fit on an integrated chip, or it could be expanded to cover the circumference of an industrial plant production room. Such an instrument would provide a sturdy, low cost, and more versatile alternative to both mirror-based CRDS and EWS detectors.

Specific Aims

The purpose of this project is to develop a rugged and versatile fiber-optic based resonator to quantitatively measure absorption of ammonia in trace concentrations. Time resolved absorption measurements will reduce most sources of noise and improve limits of detection. Techniques developed in cavity ring-down spectroscopy minimize the inherent problems with power ratio measurement, such as source fluctuations and low sample interaction. By applying evanescent wave spectroscopy through an optical fiber, cavity alignment difficulties will be eased, internal scattering concerns will be eliminated, and instrument durability will be improved.

The long-term goal of this project is to develop a practical instrument using low cost communication grade optical fiber, continuous-wave diode lasers, and inexpensive

diode detectors. The feasibility of a fiber optic ring resonator for time-resolved evanescent wave absorption measurements will be demonstrated using a distributed feedback diode laser with an acousto-optic modulator and InGaAs detector. Recent progress in continuous-wave cavity ring-down spectroscopy and telecommunications technology can be applied to this system, and an inexpensive, portable instrument devised for the measurement of a wide variety of analytes.

Experimental Design

A diagram of the proposed apparatus appears in Figure 1. Continuous-wave infrared laser light is focused through an Acousto-Optic Modulator (AOM) and a Faraday isolator, into the input fiber. The Faraday Isolator prevents back-reflections which would cause laser frequency and amplitude fluctuations. The AOM allows the deflection of the incident beam from the input fiber for measurement of the ring-down decay in the resonator. One edge of the input fiber is mounted on a translation stage within a few wavelengths of the resonator to couple light into the cavity through photon tunneling. A 3m length of bare single-mode fiber with the two ends joined by a fusion splice

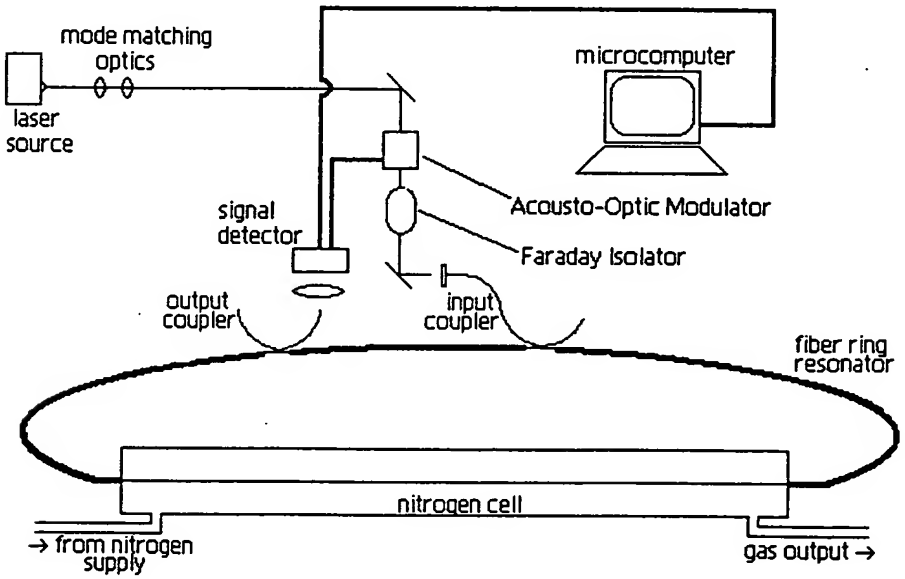


Figure 1: Design of Optical Fiber Ring-Down Resonator

forms the resonator. A 1m length of the resonator fiber, which is exposed to the core, is sealed in a nitrogen filled cell. Analyte gas can be introduced to this chamber for evanescent wave detection. At another point along the resonator ring is the output coupler. Similar to the input coupler, the output fiber couples light out of the cavity from a position a few wavelengths from the resonator and directs it toward a diode detector. The detector signals the AOM controller when a pulse of a predetermined amplitude is detected. The AOM then deflects the incident beam from the input fiber to allow the measurement of the ring-down decay. The detector also interfaces with a computer, which acquires the output voltage as a function of time and fits it to an exponential curve using a linear least squares fitting routine. The decay constant, τ, of the resonator is extracted from the fitting parameters and represents 1/e of the maximum voltage. In order to facilitate statistical analysis of the system, decay constants are averaged over 100 acquired curves taken over approximately one second.

The decay constant is related to concentration by the relationship

$$\frac{1}{\tau} = \frac{1}{\tau_0} + \alpha L$$

in which τ_0 is the intrinsic decay time of the cavity, α is the absorption coefficient of a given concentration of the absorbing molecule, and L is the length of interaction of the field with the absorber. Measurement of τ in the absence of ammonia provides the intrinsic decay time of the fiber cavity. This is accomplished by placing the cavity fiber in an atmosphere of nitrogen to obtain τ_0. The analysis is then performed in the presence of a small quantity of absorbing gas for quantitative detection. Ammonia can be bled into the nitrogen line using a drip valve, and another series of decays is taken to obtain Another method of taking τ and τ_0 that is more appropriate when it is not possible to control the quantity of ammonia is to slightly tune the wavelength of the source laser. Measurement at an off-resonance wavelength gives the non-absorbing decay constant, τ_0, while τ is obtained by tuning back to a resonance peak. Absolute concentrations can be calculated with only τ, τ_0, and the characteristics of the detected line, which are published values.[15]

Though the measurement technique is not dependent on the signal power, it remains essential that a detectable amount of power appear at the output. It is therefore

important to maximize the input power and to couple the lowest order transverse mode into the resonator. A telescopic lens system matches the laser mode to the lowest order mode of the fiber in order to enhance tunneling probability into the resonator. Single mode fiber is used to preserve the mode inside the fiber, ensuring maximum interaction of the evanescent field with the analyte.

Feasibility

The most important consideration is the minimization of optical loss in the resonator. There are several sources of attenuation that have to be addressed. Input and output coupling are similar and are an experimentally variable way to change both the loss in the resonator and the amount of power available for detection. Also important are the losses internal to the optical fiber, including bulk scattering and absorption, unwanted absorption at the fiber core's surface, and attenuation at the spliced joint.

A laser couples power into the input fiber most effectively if the light is in the lowest order transverse mode. This is achieved by using a telescopic lens system to focus the beam into the fiber. A single mode fiber is used to avoid mode scrambling, as it will only efficiently transmit the lowest order mode. The construction of the fiber complicates the mathematical description of the transverse mode. The lowest order mode is a near-Gaussian function however, and it can be effectively approximated by the lowest order Hermite-Gaussian, or TEM_{00}, mode. This is the least divergent mode; all higher order modes quickly radiate out of the fiber.[13] In addition to being the best mode for coupling into the fiber, the lowest order mode provides the most power for coupling into and out of the resonator.

Coupling efficiency, both in and out of the resonator, is analogous to the reflectivity of the mirrors in a traditional cavity ring-down experiment.[17] The loss due to coupling is directly related to the photon tunneling efficiency between the input and output coupling fibers and the resonator. The overlap coefficient is calculated by integrating the product of the two modal functions over space. It can be shown that the best overlap is achieved when both the input (or output) fiber and resonator are in the lowest mode, which is approximated by a Gaussian distribution. The combination of

single mode fiber and proper mode matching ensure good overlap and thus predictable coupling into the resonator. This improves the sensitivity of the apparatus by allowing experimental optimization of resonator loss and analyte interaction.

A calculation of mode overlap gives a value proportional to the coupling efficiency and a relative effective reflectivity in the resonator. Given that a standard single mode optical fiber is approximately 8.2 μm in diameter,[18] assuming a measurement wavelength of 1550 nm and negligible fiber separation, one can calculate a tunneling coefficient of 0.0632. This value can be adjusted between over 50% to 0% efficiency by changing the separation of the fibers, thus decreasing the tunneling coefficient. Appendix I gives a detailed approximation of the overlap. Because coupling can be experimentally tuned, this apparatus is limited not by the efficiency of the couplers but by the internal loss of the fiber. Using this property, it is possible to calculate some important resonator characteristics. Ignoring internal sources of loss in the resonator and assuming coupling of 44.5×10^{-6}, a bandwidth of 3.45 kHz is calculated from a free spectral range of 226 MHz and a finesse of 70596. These values can be optimized by changing the fiber separation to experimentally minimize resonator loss while maximizing detector response.

There are other sources of loss, besides the absorption of the analyte, that lie in the properties of the optical fiber. The use of commercially available low loss fibers and a fusion splice to form the ring keep the intrinsic attenuation in the resonator acceptable for sensitive detection. Standard communication grade optical fiber is available with specified maximum attenuation of 0.19 dB/km at 1550 nm.[18] A typical fusion splice adds another 0.02 dB, which can be improved by careful core alignment and fiber preparation.[19] Including these losses in the resonator characterization, a calculation yields a bandwidth of 344 kHz and a calculated τ_{empty} of 4.63×10^{-7} s. This value remains sufficiently low for the desired detection limits, but it can be improved by careful splicing technique or increased fiber length.

Previous efforts at detection of ammonia through the use of resonant cavities show very low limits of detection.[4,5,20] This is based in part on the device and in part on the vibrational transition that is monitored. Several strong absorption lines exist around 1550 nm in the $2\nu_3$ vibrational overtone, the most suitable of which is the $^{P}R_0$ transition,

centered at 1551.96 nm[15] because of its strong intensity and good separation from nearby lines. The characteristics of this transition allow the calculation of a theoretical detection limit of 0.189 ppb based on the calculated resonator properties. Appendix II details this calculation. This sensitivity is comparable to current CRDS measurements and can be improved by minimization of the splicing loss.

A fiber optic based device is only recently possible because of technological improvements in fiber attenuation through reduction of bulk loss and better splicing techniques. Detection of ammonia at telecommunication transmission wavelengths is well documented for a CRDS spectrometer and will be reasonably accomplished by this new device. Many problems encountered in a traditional ring-down spectrometer are solved by this technique. Broadband tunability is accomplished due to the low loss characteristics of optical fibers over a wide spectral range. The use of fiber optics increases the durability of the apparatus and reduces the cost of materials. Mode matching difficulties usually encountered by a mirror based resonant cavity are eased by single mode fiber technology. Resonator coupling loss is adjustable through mechanical alignment of the photon tunneling distance. The main limitation in achieving the theoretical limit of detection is attenuation introduced by the fusion splice, but it is possible to control this loss by accurate cleaving and careful core alignment. We believe this experiment will successfully combine EWS and CRDS to produce a sensitive, yet rugged instrument.

Progress Report

A large percentage of Professor Lehmann's research group's efforts center on trace detection of gases through cavity ring-down spectroscopy (CRDS). Previous work focused on observation of weak overtone bands of HCN with pulsed laser CRDS[2,3] and development of a continuous-wave (CW) CRDS device for the detection of trace quantities of H_2O.[4] In an effort to extend the CW-CRDS technique to a broader range of molecules, a similar apparatus was contructed to detect ammonia.[4,20] Current work

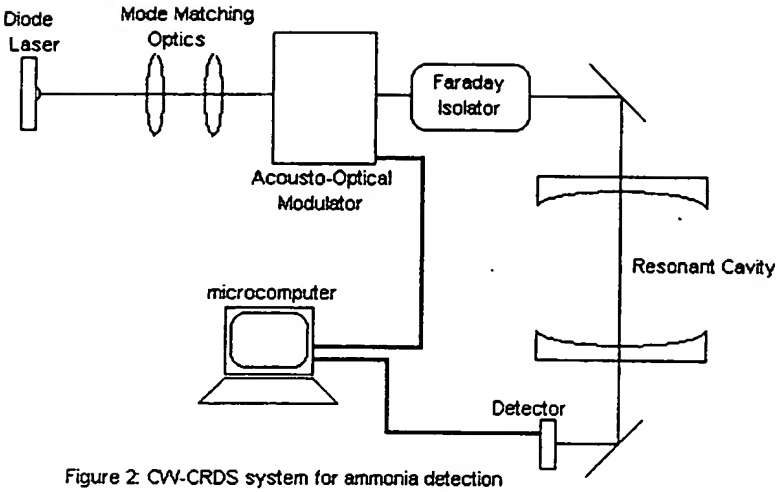


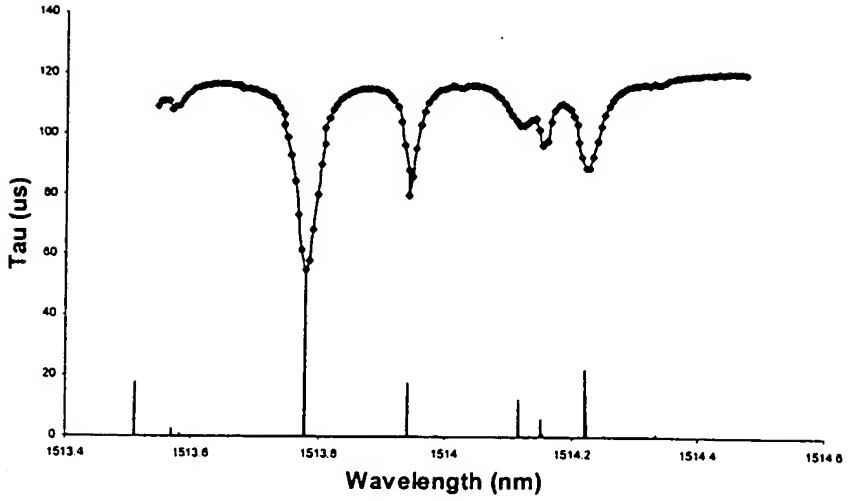
Figure 2: CW-CRDS system for ammonia detection

includes optimization of the CW-CRDS system and development of a prism based resonator patented by Professor Lehmann and Dr. Paul Rabinowitz.[21]

My work to date is divided between two projects, one of which is the CW-CRDS resonator for trace detection of water and ammonia. The spectrometer consists of a diode laser which couples light through a mode matching telescope, an Acousto-Optic Modulator (AOM), and a Faraday isolator into a cavity formed by two highly reflective mirrors. The AOM temporarily deflects the light away from the cavity when triggered by the ring-down detector, so it allows light to escape the resonator before another pulse is introduced. The Faraday isolator prevents back-reflections from the input mirror of the resonator from returning to the laser, since feedback causes instability in laser frequency and amplitude. A diagram of this apparatus appears in Figure 2.

John Dudek, a former graduate student in the Lehmann group, did significant work on this apparatus in collaboration with Win-Ben Yan and Armando Velasquez, both of Meeco, Inc. They showed the device to be capable of detecting water as low as 1.51 ppb in nitrogen, with a theoretical detection limit of 100 pptv.[4] The theoretical limit was not reached because of apparatus limitations for producing low ammonia concentrations. John Dudek also worked to extend the functionality of the spectrometer to other molecules. Using a similar device, he detected ammonia at a concentration of 1.51 ppb in nitrogen and calculated a theoretical limit of detection of 900 pptv.[4] My work on this project involved refinement of the ammonia measurement, detection of water with the

Figure 3: Detection of Water around 1514 nm
(calculated lines appear on x-axis)



ammonia device, and detection of acetylene in nitrogen at the same wavelength. A water spectrum appears in Figure 3, along with calculated water lines.[23]

The other project on which I worked is a prism based resonator conceived by Professor Lehmann and Dr. Paul Rabinowitz. This device uses two roof angle prisms to form a resonator. The sides of the prisms that face the cavity are aligned near Brewster's angle to minimize reflection loss.[21] This apparatus is more versatile than a traditional CRDS resonator for several reasons. The prisms do not have the narrow bandwidth limitations of mirrors; they transmit through most of the visible and near-infrared region. The faces of the prisms, while important to the quality of the resonator, are not significantly susceptible to corrosion. The inside of the cavity can therefore be exposed to analytes that would damage dielectric mirror coatings, such as corrosive gases. The prism materials, however, require expensive superpolishing and precise cutting for use in such a resonator. A diagram of the prism resonator appears as Figure 4.

Greg Engel, a former undergraduate student in the Lehmann group, worked on the Brewster's angle prism cavity using fused silica prisms. He demonstrated the feasibility of such a resonator by measuring the empty cavity loss, τ_{em}, as a function of wavelength.[22] My work with this device principally involves characterization of new materials for prism construction. Fused silica is highly susceptible to birefringence, which is an undesirable property because the Brewster's angle reflection, and thus the

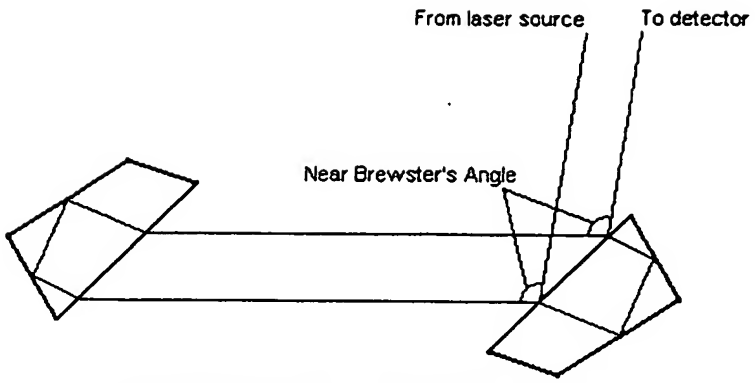


Figure 4: Diagram of Brewster's Angle Prism Resonator

cavity loss, is highly dependent on polarization. A fused silica prism is difficult to properly use in the resonator without causing stress-induced birefringence and affecting the Brewster's angle reflection, resulting in higher cavity loss. In the same way, it is not suited for use in a high pressure cell. The desired characteristics of potential materials I have studied include non-unique optical crystal axes (which may lead to birefringence), broad transmission spectra, and the ability to be superpolished. Successful identification of new materials will allow construction of lower loss prisms, facilitating higher cavity finesse and lower limits of detection. Thus far, I have investigated the loss characteristics of samples of undoped YAG ($Y_3Al_5O_{12}$), sapphire (Al_2O_3), calcium fluoride, and barium fluoride with a CRDS device. Future efforts will include conclusion of material analyses, production of a better prism based resonator, and real time detection of multiple analytes at several different wavelengths.

The two ongoing projects in the Lehmann group conceptually point to the development of a low cost, broadband, rugged CRDS spectrometer. These qualifications are supported by current fiber optics technology. The Lehmann group demonstrated the feasibility of a CW-CRDS detector for ammonia and of a broadband non-mirror based cavity. Future work will emphasize extension of current CRDS methods to the development of a more durable and less expensive instrument based on fiber optics technology.

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Appendix I: Calculation of photon tunneling efficiency

The tunneling efficiency is proportional to the overlap of the excited modes in the propagation media. In the case of the optical fiber resonator, single mode fiber is used in which only the lowest order mode is excited. The efficiency is thus proportional to the overlap of the lowest order mode of the input fiber and the resonator fiber. This is calculated below to find an efficiency proportional to 44.5 ppm based on a fiber separation of 7.5 μm at a wavelength of 1.55μm.

The boundary conditions implicated by a step index fiber complicate a description of the transverse mode of light. The use of single mode fiber allows only the lowest order mode to propagate. Although this mode is described by a combination of Bessel functions, it is sufficiently approximated by the Hermite-Gaussian TEM_{00} mode.[13]

The TEM_{pq} mode, where p and q are the mode indices, is described by[24]

$$E_{pq}(x,y) = H_p\left(\frac{\sqrt{2}x}{w}\right)H_q\left(\frac{\sqrt{2}y}{w}\right)e^{-(x^2+y^2)/w^2}$$

where $H_p(u)$ and $H_q(u)$ are the associated Hermite Polynomials of order p and q, respectively, and w is the laser spot size. For a single mode fiber, the transverse mode is approximated by the TEM_{00} mode, with $p = q = 0$. In this case, $H_0(u) = 1$, so

$$E_{pq}(x,y) = e^{-(x^2+y^2)/w^2}$$

The function is not normalized, so a normalization constant must be calculated.

$$\int_{-\infty}^{\infty}\int_{-\infty}^{\infty} N^2 e^{-2(x^2+y^2)/w^2}\,dxdy = 1$$

Integrating, we find $N = 1/w\sqrt{2/\pi}$. The waist size, w, is approximated from the definition of numerical aperture. Numerical aperture (NA) is the maximum cone angle of light the fiber can accept; it is calculated from the indices of refraction of the core and cladding. The waist is calculated from the NA to be 3.49 μm, using[25]

$$\tan\left(\sin^{-1} NA\right) = \frac{\lambda}{\pi w}$$

It is substituted into the Gaussian mode approximation. The coordinates are translated such that the origin is at the center of the target fiber. The fibers are separated by a distance, d_0, and have radii r_1 and r_2, corresponding to the input and target fibers, respectively. An integration is performed over all space to find the total mode overlap:

$$\int_{-\infty}^{\infty} N^2 e^{\frac{(x^2+y^2)^2}{w^2}} e^{\frac{((x-(r_1+r_2)-d_0)^2+y^2)}{w^2}} dxdy$$

This calculation yields a coupling efficiency proportional to 44.5 x 10^{-6} from two fibers 8.2μm in diameter separated by an additional 7.5μm. Figure 4 shows a plot of the overlapped functions.

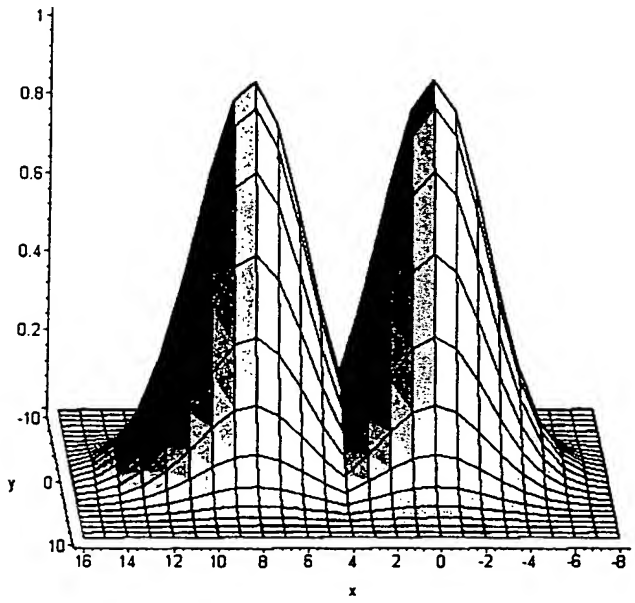

Figure 4: Overlap of two single mode optical fibers of radii = 4.1 μm with no additional separation (x,y in μm)

Appendix II: Calculation of theoretical detection limit

This section describes the lowest detectable concentration of ammonia in the 1550 nm region with the fiber-based resonator in the shot noise limited case.

Convention dictates that twice the standard deviation of a measurement represent the theoretical limit of detection. Romanini and Lehmann[3,17] represent the standard deviation of the detected absorption coefficient in the shot noise limited case as

$$\sigma_\alpha = \frac{1}{l\sqrt{QN_0}}\sqrt{\frac{\Delta\upsilon}{FSR}}\sqrt{\frac{(T+L)^3}{T^2}}$$

where l is the resonator length, T is the transmittivity of the mirrors, L is the additional loss in the resonator, Q is the quantum yield of the detector, N_0 is the number of photons striking the resonator input, $\Delta\nu$ is the linewidth of the input and FSR is the free spectral range of the resonator, calculated by c/(nd), where c is the speed of light in vacuum, n is the index of refraction in the resonator, and d is the distance of one round trip in the ring. The standard deviation of the absorption coefficient, α, is calculated and related to an absolute concentration of ammonia.

Calculation of $\Delta\nu$

The bandwidth of the input is best calculated by a convolution of the laser linewidth and the cavity bandwidth. This is approximated by the square root of the sum of the squares of the two values. Diode laser linewidths are often on the order of 1MHz.[4] The resonator bandwidth is calculated from the finesse ($\pi R^{1/2}/(1-R)$), where R is the loss in round trip transmission of the resonator. This is found to be 660 assuming coupling of approximately 40 ppm, and typical fiber loss of 0.19 dB/km (131 ppm/3m) and 0.02 dB/splice (4100 ppm). The free spectral range calculated from the above expression is 226 MHz. This gives a resonator bandwidth of 344 kHz. This results in a $\Delta\nu$ of 1.06×10^6.

Estimation of resonator loss

The transmittivity of the resonator is analogous to the tunneling efficiency of the input and output couplers. The balance between coupling and detection response is achieved when $2T = L$.[17] The significant sources of loss in the resonator are the bulk attenuation of the fiber and the splicing loss. Standard single mode fiber[18] has specified loss of 0.19 dB/km, which corresponds to a loss of 131 ppm over a 3 m resonator length. A typical fusion splice[19] attenuates 0.02 dB, or 4600 ppm. These numbers are combined to give a loss of $L = 4731 \times 10^{-6}$. We will take $T = L/2 = 2366 \times 10^{-6}$.

Determination of detector response

The threshold power of typical optical fibers is on the order of 10 mW before performance is compromised. For 1 second of detection at 10 mW of power, 7.5×10^{16} photons are introduced to the resonator. In order to determine the QN_0 product, the quantum yield of the detector must also be calculated. A typical InGaAs photodiode detector has a quantum yield of 0.745 electrons/photon. This corresponds to a QN_0 product of 5.58×10^{16}.

From the above information, the standard deviation in a detectable absorption coefficient is 2.44×10^{-13} /cm. This must be further corrected to reflect evanescent detection. The majority of the field propagates in the fiber and only a small percentage exists in the evanescent field for interaction with the absorber. This percentage is calculated by finding the ratio of the Bessel functions describing the confined and evanescent fields. The percentage is determined to be 4.5%, giving a limit of detection of 1.09×10^{-11} /cm in 1 second. This can be further related to an absolute concentration.

Calculation of detectable concentration

Typcially, CRDS measurements yield an absorption coefficient, which is then converted to a concentration. A similar calculation is done using twice the standard deviation of a detectable absorption coefficient as the theoretical limit of detection. This was calculated to be 1.09×10^{-11}/cm. The strength, S, of the monitored ammonia line is

0.7000×10^{-4} $cm^{-1}torr^{-1}$. The smallest measurable α can be converted to a partial pressure using

$$\alpha_{lim} = P_{lim} S$$

The partial pressure of ammonia corresponding to α_{lim} is 1.55×10^{-7} torr, or 2.04×10^{-10} atm. This can be converted to a number of molecules per unit volume:

$$\frac{P_{lim} V}{RT} \times N_A = N_{lim}$$

where V is a unit volume, R is the ideal gas constant, T is the temperature in Kelvin, and N_A is Avagadro's number. The number of molecules in 2.04×10^{-10} atm of ammonia is 5.02×10^{9}/mL. This is compared to the number of molecules at standard temperature and pressure, 2.66×10^{19}/mL:

$$\frac{5.02 \times 10^{9}}{2.66 \times 10^{19}} * 1 \times 10^{9} = 0.189 ppb$$

Therefore, in one second, 0.189 ppb ammonia can be detected in the shot noise limited case.

PRINCETON UNIVERSITY – THE GRADUATE SCHOOL – 201 NASSAU HALL

GENERAL EXAMINATION REPORT
(PH.D. CANDIDATES ONLY)

TO: Dean of the Graduate School DATE: May 4, 2001

FROM: Department of Chemistry

CONCERNING: Tarsa, Peter [redacted]
(Last Name First MI) (Social Security Number)

(This report should be returned to the Graduate School Office within one week after the General Examination.)

Principal members of the examination committee were:

Professors Bernasek, Warren, Car and Lee

NOTE: The examination committee must consist of at least three members, at least two of whom shall normally hold the rank of assistant professor or higher on the faculty of Princeton University.

This General Examination was given during the authorized examination period in: (circle one)

OCTOBER JANUARY (MAY)

and graded as follows according to the appropriate scale:

I. (Passed) Failed II. A B C D F

I. ☒ In the judgment of the department, the above-named candidate has passed the General Examination and may advance to the Ph.D. degree.

II. ☐ The candidate has passed the General Examination but is not recommended for continued Ph.D. degree candidacy. The candidate is therefore recommended for a terminal Master's degree and has been so informed. A brief estimate of the quality of the candidate's performance follows:

_____

_____

_____

III. ☐ The candidate has failed the General Examination and has been so informed. A report of the quality of the candidate's performance follows:

_____

_____

_____

_____

Because of this failure, the student's status is in question. Please give us the department's recommendation regarding continued enrollment and support:

_____

_____

M Semmelhack
(Signature) Director of Graduate Studies

Graduate School Office, White Copy; Department, Yellow Copy; Student, Green Copy